



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: <b>PCT/US98/25045</b></p> <p>(22) International Filing Date: <b>24 November 1998 (24.11.98)</b></p> <p>(30) Priority Data: <b>60/066,307</b>      <b>25 November 1997 (25.11.97)</b>      <b>US</b></p> <p>(71) Applicant (for all designated States except US): <b>JOHN HOPKINS UNIVERSITY [US/US]; 3400 North Charles Street, Baltimore, MD 21218-2695 (US).</b></p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): <b>WEIHS, Timothy, P. [US/US]; 3422 University Place, Baltimore, MD 21218 (US). MANN, Adrian, B. [US/US]; Apartment K1, 106 W. University Parkway, Baltimore, MD 21209 (US). SEARSON, Peter, C. [US/US]; 2330 Bright Lead Way, Baltimore, MD 21209 (US).</b></p> <p>(74) Agent: <b>OLIVER, Eric; Dickstein Shapiro Morin &amp; Oshinsky LLP, 2101 L Street, N.W., Washington, DC 20037-1526 (US).</b></p>		<p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: <b>ELECTROCHEMICAL-CONTROL OF ABRASIVE POLISHING AND MACHINING RATES</b></p> <div data-bbox="440 1163 1192 1661"> <p><b>POLISHING (CMP OF METALLIZATION)</b></p> <p><b>ABRASIVE PAD 9</b></p> <p><b>10 POLISHING SLURRY AND ELECTROLYTE</b></p> <p><b>5</b></p> <p><b>11 METALLIZATION 11 OXIDE OR SURFACE LAYER PROPERTIES CONTROLLED ELECTROCHEMICALLY</b></p> </div> <p>(57) Abstract</p> <p>An apparatus and method is disclosed, both of which use electrochemistry to selectively grow and remove hard oxide coatings on metals, and capacitive double layers on non-metals and semiconductors, in order to predict and control the rate of surface abrasion during planarization of the surface of such materials. The apparatus includes a potentiostat or other power supply (1) for applying an electrical potential to the surface of the sample (5). The apparatus also employs a reference electrode (2) and a counter electrode (3). In one embodiment, an abrasive pad (9) and polishing slurry and electrolyte (10) are used to abrasively wear the surface of a metallization layer (11) on the sample (5). A voltage is applied to the metallization layer (11) in order to control the oxide or surface layer properties during chemical mechanical polishing.</p>		

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## ELECTROCHEMICAL-CONTROL OF ABRASIVE POLISHING AND MACHINING RATES

5           This application derives and claims priority from provisional U.S. patent application no. 60/066,307, filed November 25, 1997, which is incorporated herein by reference.

### BACKGROUND OF THE INVENTION

10           In the process of semiconductor fabrication, layers of material are deposited onto substrate surfaces to form interconnects. Excess layer material is removed so that a further level of interconnects may be placed on top of the material. In this way, many layers can be created. In such structures, however, the topography of each layer must be precisely controlled so that successive layers and photolithographic processes can be accurately applied.

15           A process known as planarization is performed on the surface of each layer to prepare the surface of each layer for subsequent levels. Currently, surface planarization is achieved using mechanical polishing, mechanical machining, and chemo-mechanical polishing (CMP).

20           Mechanical polishing, for example, utilizes an abrasive material, typically in the form of a pad or slurry, which is moved repetitively over the surface to be

polished. This causes small particles of the surface to be removed from the highest surface features while the lower features remain relatively untouched. In this way, a high degree of planarization is achieved.

Mechanical machining, on the other hand, involves the selective removal  
5 of material from specific sites by the application of a hard, abrasive machining piece, as used for instance in a lathe.

Both mechanical machining and mechanical polishing involve the mechanical breaking of bonds between the material being abraded and the surface itself. At present, the success of each of these methods is limited since there is no  
10 way of controlling the hardness of the surface being planarized. Rather, planarization is currently achieved by controlling the abrasive qualities of the polishing pad or slurry. This allows for only an indirect control of the planarization. As an example, Murarka et al. (U.S. Patent No. 5,637,185) teaches measuring the electrical potential of the slurry in order to detect the end of the polishing process. Similarly, Tsal et al.  
15 (U.S. Patent No. 5,575,706) teaches the utilization of electric fields to control the density of the abrasive slurry particles between the polishing pad and the Si-wafer. In addition, Kishii et al. (U.S. Patent No. 5,562,529) teaches the use of electrochemistry to increase the density of ions in the slurry.

In yet another method of effecting planarization, chemo-mechanical  
20 polishing (CMP) uses chemical means to break chemical bonds at the surface during polishing or machining of a surface. Similar to the mechanical methods, CMP is currently limited since there is presently no way of controlling the hardness of the

surface being planarized. Rather, CMP processes rely upon measuring the rate of surface layer formation, dissolution rates, and rate of chemical acceleration of polish rates in order to control surface planarization. *Surface Layer Formation During The Chemical Mechanical Polishing of Copper Thin Films*, J.M. Steigerwald et al., MRS Symp. Proc. 337, 133, 1994; *Mechanisms of Copper Removal During Chemical Mechanical Polishing*, J.M Steigerwald, J. Vac. Sci. Tech. B 13, 2215, 1995. In addition, other chemical techniques, as taught by Chen, (U.S. Patent No. 5,637,031) control slurry density and wear rates using the addition of ions from a variety of elements. *Effect of Copper Ions in The Slurry on The Chemical-Mechanical Polish Rate of Titanium*, J.M Steigerwald et al., J. Electrochem. Soc. 141, 3512, 1994; *The Effect of The Polishing Pad Treatments on The Chemical-Mechanical Polishing of SiO<sub>2</sub> Films*, W. Li, D.W. Shin et al., Thin Solid Films 270, 601, 1995; *Electrochemical Potential Measurements During The Chemical-Mechanical Polishing of Copper Thin Films*, J.M. Steigerwald et al., J. Electrochem. Soc. 142, 2379, 1995.

Each of these CMP methods are limited in controlling planarization as they do not allow for the direct control of the surface wear properties of a surface being planarized.

#### SUMMARY OF THE INVENTION

It is an object of the invention to provide the ability to control or inhibit wear on the surface of a material such as a semiconductor.

Another object of the invention is to control the surface conditions of a material such as a semiconductor using electrochemistry.

Yet another object of the invention is to control the wear rate of the semiconductor material using electrochemistry.

5           The present invention accomplishes the above and other objects and advantages by providing a method of and apparatus for using electrochemistry to selectively grow or remove oxide coatings on metals or to create a capacitive double layer on non-metals in order to directly control the surface wear properties of a surface being planarized.

10           For many materials, the application of an electric potential to the surface when it is immersed in an electrolyte permits the controlled growth of a surface layer.

          According to the present invention, the chemical and physical properties of a surface (e.g., hardness of a surface, oxide composition, etc.) and its rate of abrasive wear are directly linked so that the electrochemical growth of the oxide layer and the  
15          creation of a double capacitive layer provides a means to control the wear rate of the surface.

### BRIEF DESCRIPTION OF THE DRAWINGS

          The foregoing and other objects and advantages of the present invention will become more apparent from the detailed description of the preferred  
20          embodiments of the present invention given below with reference to the accompanying drawings in which:

FIG. 1(a) shows the formation of a surface layer of oxide film on a metallic system;

FIG. 1(b) shows the generation of a capacitive double layer of oxide film;

5           FIG. 2(a) shows where the oxide thickness at a specified voltage is measured;

FIG. 2(b) shows the mechanical hardness of the metal surface with the oxide present versus the voltage at which it was grown;

10           FIGS. 3(a) and 3(b) show the utilization of a conductive machine tool in accordance with the invention;

FIG. 4 shows the use of the invention with mechanical polishing;

FIGS. 5(a) and 5(b) show use of the invention with chemo-mechanical polishing (CMP); and

15           FIG. 6 shows the occurrence of dishing and cusp formation in metallization.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will be described in detail as set forth in the preferred embodiments illustrated in FIGS. 1-6. Although these embodiments  
20       depict the invention in its preferred application to specific semiconductor materials, it should be readily apparent that the invention has equal application to any type of material that encounters the same or similar problems.

FIG. 1(a) is a schematic view of an apparatus 12 for the controlled growth of an oxide layer 6. The apparatus 12 includes a potentiostat 1 (or other power supply) for applying an electrical potential to the surface of the sample 5. The potentiostat 1 applies the desired voltage to the sample 5 such that the sample 5 operates as a working electrode in the standard three electrode cell model. The apparatus also employs a reference electrode 2 and a counter electrode 3, both of which are immersed in the electrolyte 4 (or other known aqueous solution or bath). The reference and counter electrodes are used to assist in measuring and maintaining the desired electrical potential on the sample 5 when it is immersed in electrolyte 4.

In metallic systems (e.g., Ni, W, Ta, Al, Cu, Mo, etc.) the surface layer may be an oxide film, which can be in the form of either a porous layer or a fully dense barrier layer dependent upon the composition of the electrolyte and the voltage potential applied. For other conductive materials which do not have a native oxide, as well as semiconductors (such as, for example, Si and GaAs), the application of an electric potential can lead to the generation of a capacitive double layer at the surface, and eventually, at large potentials, an oxide film will develop. The presence of a wear resistant surface layer, in the form of both oxide films and capacitive double layers, modifies the abrasive wear properties of a surface and, as a consequence, electrochemistry provides a direct means by which to control the wear rate of a surface during mechanical polishing and machining. This controlled application of voltage permits the controlled growth of the oxide layer 6, as shown in FIG. 1(a). In metallic systems (such as, for example, Ni, W, Ta, Al, Cu, Mo, etc.), the oxide layer 6 may be in the form of either a porous layer or a fully dense barrier layer dependent



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upon the composition of the electrolyte and the voltage potential applied. Where the sample 5 is a conductive material that has no oxide film layer or the sample is a semiconductor such as Si or GaAs, a capacitive double layer 7 is formed at the surface of the material, as shown in FIG. 1(b).

5           In accordance with the invention, the growth and characteristics of the oxide layer on such metals (e.g., Ta (tantalum)) is controlled. In particular, the thickness of the oxide can be increased (or decreased) with a corresponding proportional increase (or decrease) in the applied voltage, as shown in FIG. 2(a). In addition, the variation of the voltage proportionally affects the hardness of the  
10   surface, as shown in FIG. 2(b). (In FIG. 2(a), the oxide thickness at a specified voltage is measured by two different methods: coulometric and potentiostatic. The two methods give different absolute values for the thickness because they use different constants in their calculations.)

          Applying the relationships illustrated in FIGS. 2a and 2b, manipulation of  
15   the voltage through the potentiostat 1 allows for the growing of oxides of a predetermined thickness and hardness. Inasmuch as the hardness of a surface and its rate of abrasive wear are directly linked, the electrochemically controlled growth of the oxide layer provides a reliable mechanism to control the wear rate of the surface.

          As shown in FIG. 3(a), the invention can be readily applied to mechanical  
20   machining procedures. Here a voltage is applied not to the surface of the sample 5 being machined but to the machine tool 8 itself. When using such a conductive machine tool piece 8, the cutting surface of the machine tool can be controlled to

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minimize the wear of the machine tool and simultaneously enhance the rate of abrasion of the surface of the sample 5 being machined.

In the alternative, as shown in FIG. 3(b), where the sample 5 being machined is conductive, the invention can be used by applying the voltage across the sample 5 itself to grow an oxide or capacitive layer 6 on the sample 5.

FIG. 4 illustrates another embodiment of the present invention in which the above technique is used in the specific application of mechanical polishing. In this embodiment, an abrasive pad 9 is used in place of the machine tool piece 8 in order to less abrasively wear the substrate surface 6.

FIG. 5(a) illustrates another embodiment of the present invention in which the application of voltage to the metallization layer is used in conjunction with the chemo-mechanical polishing (CMP) of metallization. In this embodiment, a polishing slurry and electrolyte 10 are used to abrasively wear the surface of metallization layer 11, which has been added to substrate 5. A voltage is applied to metallization layer 11 in order to control the oxide or surface layer properties during the CMP process and in accordance with the invention.

As shown in FIG. 5(b), by making the metallization layer 11 the working electrode of a standard three-electrode cell, in accordance with the invention, a barrier surface oxide layer 6 can be grown on metallization layer 11. This lowers the rate of abrasive wear at the metal's surface. Thus, using the invention in conjunction with a CMP process, for instance, in the fabrication of an integrated circuit upon a

Silicon wafer, the oxide 6 can be selectively grown and removed during the polishing process to either decrease or increase the rate of polishing.

As an example, during the initial stage of the polishing, the oxide 6 could be removed to increase the speed of the polishing process, but then re-grown when  
5 the metallization layer 11 is very thin, so as to ensure that the final stages of the polishing process produce a highly planar surface. Having the wear resistant oxide layer 6 present during the final stages of the polishing process will improve the local planarization (i.e., the surface is level over very small areas (on the order of micrometers)) as the metal interconnects will be less likely to suffer from the dishing  
10 12 or cusp 13 formation problems as shown in FIG. 6.

It is important to realize that the processes described throughout this disclosure are simply a few examples and preferred embodiments describing how electrochemistry can be used to engineer a surface with specific wear properties. During many other processes involving planarization, the same basic technique can  
15 be used to control abrasive wear.

Additionally, it should be stated that the technique is not restricted to metallic systems with a native oxide layer and, as stated previously, it can be utilized with metallic systems where there is no native oxide, and also with non-metallic conductors, such as semiconductors and high-temperature superconductors. For  
20 metals which do not have a native oxide, electrochemistry can be used to artificially create an oxide layer. For both non-metals and metals, electrochemistry provides a way to vary the size of the capacitive double layer which develops at the surface.

Modifying the double layer permits the adhesive force between two contacting surfaces to be varied and so provides a way to reduce or increase the force applied at an abrasive contact. This in turn permits the rate of wear of a surface to be controlled.

5           Although the invention has been described in terms of the particular apparatus embodying the invention, the method steps required to make and use the apparatus are readily apparent to those of ordinary skill in the art merely from the description of the apparatus itself.

10           While the invention has been described in detail in connection with the preferred embodiments known at the time, it should be readily understood that the invention is not limited to such disclosed embodiments. Rather, the invention can be modified to incorporate any number of variations, alterations, substitutions or equivalent arrangements not heretofore described, but are commensurate with the spirit and scope of the invention. For example, instead of the standard three-  
15   electrode cell used to control growth of oxides or capacitive layers, a two-electrode cell or equivalent construction may similarly be used to obtain the same effects described herein.

What is claimed is:

1. A method of controlling treatment of a material, the method comprising the steps of:

developing a wear resistant surface layer so as to contact a surface of the  
5 treated material; and

removing portions of the treated material using a mechanically applied force during development of the wear resistant surface layer.

2. The method as recited in claim 1, wherein said developing step includes the substep of growing an oxide film as the wear resistant surface layer, and wherein  
10 said removing step includes planarization of the surface of the substrate.

3. The method as recited in claim 2, wherein said removing step includes planarization employing mechanical machining as the mechanically applied force.

4. The method as recited in claim 2, wherein said removing step includes the planarization of the treated material using mechanical polishing as the mechanically  
15 applied force.

5. The method as recited in claim 2, the method further comprising the steps of:

placing the treated material in an aqueous solution;

placing a first electrode in the aqueous solution; and

5 placing a second electrode in electrical contact with the treated material;

wherein said developing step comprises the substep of applying a voltage on the second electrode to facilitate growth and removal of the wear resistant surface layer in accordance with the increase and decrease of voltage applied to the second electrode.

10 6. The method as recited in claim 1, wherein said developing step comprises the substep of removing the wear resistant surface layer while removing portions of the treated material using the mechanically applied force.

7. The method as recited in claim 1, wherein the treated material is a material comprised of semiconductor material.

8. The method as recited in claim 1, wherein the treated material is deposited on a substrate and the treated material is comprised of a conductive material which does not have a native oxide.

9. The method as recited in claim 8, wherein said developing step comprises  
5 the substep of growing a capacitive double layer as the wear resistant surface layer.

10. The method as recited in claim 1 further comprising the steps of:

placing the treated material in an electrolytic solution;

placing a machine tool into the electrolytic solution in proximity to an area for treatment on the treated material; and

10 applying a voltage potential to a cutting surface of the machine tool;

wherein said developing step comprises the substep of developing the wear resistant surface layer on the cutting surface of the machine tool.

11. A method of treating a surface of material on a silicon wafer, the method comprising the steps of:

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placing the silicon wafer in an electrolytic bath;

placing reference and counter electrodes in the electrolytic bath;

connecting a working electrode to the material on the silicon wafer to be planarized;

5                    applying a voltage to the working electrode so as to control growth and removal of a wear surface layer formed on the material; and

planarizing the material and the wear surface layer formed on the material.

12.    The method as recited in claim 11, wherein the wear surface layer is in the  
10    form of an oxide and wherein said step of applying a voltage includes the substep of increasing the voltage relative to the reference electrode so as to increase thickness of the oxide formed on the material.

13.    The method as recited in claim 12, wherein said step of applying a voltage  
includes the substep of decreasing the voltage relative to the reference electrode so as  
15    to decrease hardness of the oxide formed on the material.



15

14. The method as recited in claim 11, wherein said step of planarizing the material includes the substep of chemo-mechanically polishing the material and the wear surface layer formed on the material so as to prepare a substantially planar surface.

5 15. An apparatus for use in controlling wear rate of a treated surface of material, the apparatus comprising:

an electrolytic solution in which the treated surface of material is submersed;

a mechanical implement submersed in said electrolytic solution, said mechanical implement applying a mechanical force on the treated surface of material;

10 and

a voltage applicator;

wherein said voltage applicator applies a voltage in said electrolytic solution to facilitate growth and removal of a film so as to contact both the treated surface of material and also said mechanical implement during application of the mechanical force on the treated surface.

15

16. The apparatus as in claim 15, wherein said mechanical implement comprises a machine tool immersed in the electrolytic solution, the machine tool being coupled to said voltage applicator to permit development of the film on a surface of the machine tool.

5 17. The apparatus as in claim 15, wherein the material is a conductive substrate, and wherein said voltage applicator is coupled to the conductive substrate and the film is developed on the treated surface of the conductive substrate.

18. The apparatus as in claim 15, wherein said mechanical implement further comprises:

10 an abrasive pad, said abrasive pad being immersed in the electrolytic solution;  
and

a polishing slurry, said polishing slurry being applied to a surface of said abrasive pad so as to contact the film and treated surface of material when said mechanical implement applies the mechanical force.

15 19. A system for using chemo-mechanical polishing (CMP) to planarize a surface of a metal interconnect applied during fabrication of an integrated circuit upon a silicon wafer, the system comprising:

an electrolytic bath, wherein the silicon wafer is immersed in said electrolytic bath during CMP;

an abrasive pad, wherein said abrasive pad applies a mechanical force on the surface of the metal interconnect while immersed in the electrolytic bath during  
5 CMP;

a polishing slurry, said polishing slurry being immersed in the electrolytic bath, and being applied to a surface of the metal interconnect; and

a power source applying a controlled voltage to said electrolytic bath during CMP, said power source further comprising:

10 a working electrode coupled to the surface of the metal interconnect;

a reference electrode, said reference electrode being immersed in the electrolytic bath; and

a counter electrode, said counter electrode being immersed in the electrolytic bath;

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wherein the controlled voltage is applied across said working and reference electrodes as increased and decreased voltages to respectively facilitate growth and removal of a polishing surface layer formed on the surface of the metal interconnect during CMP.

- 5        20.    The system as recited in claim 19, wherein the polishing surface layer comprises a layer of oxide formed between the surface of the metal interconnect and the polishing slurry during CMP.

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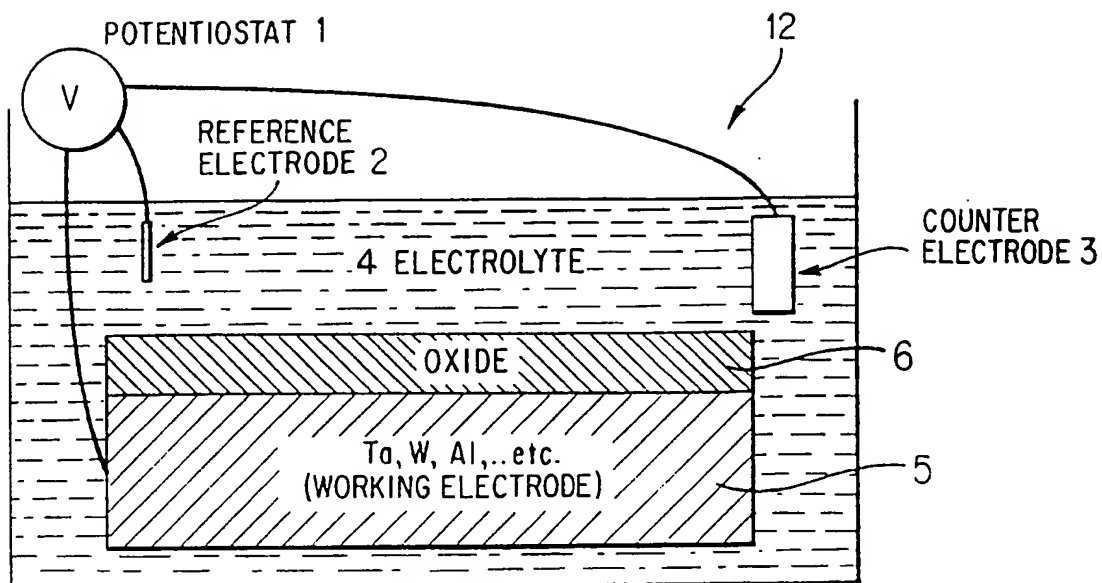


FIG. 1(a)

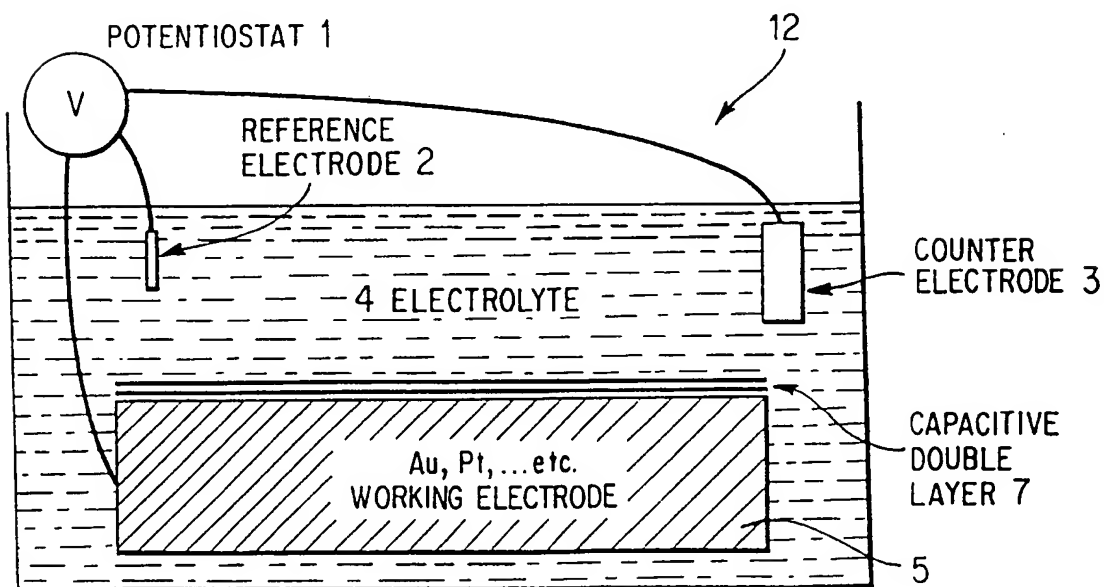


FIG. 1(b)

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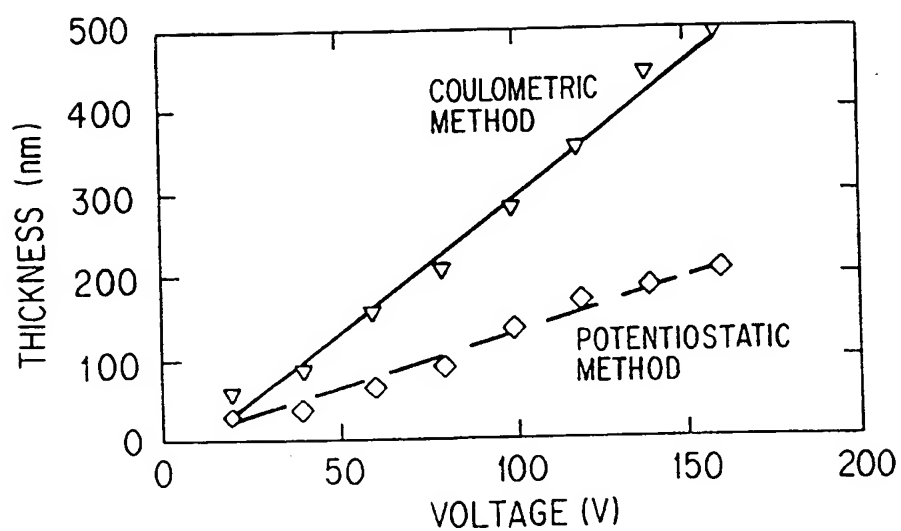


FIG. 2(a)

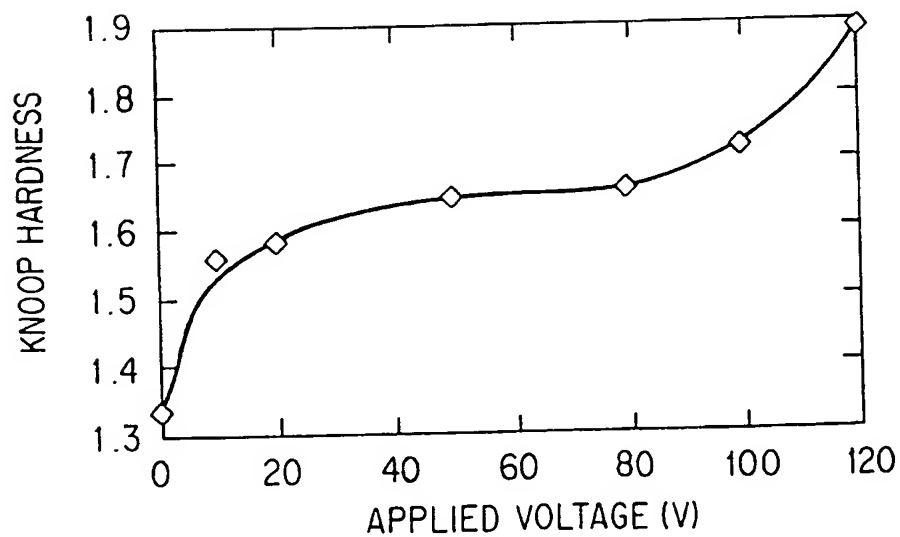


FIG. 2(b)

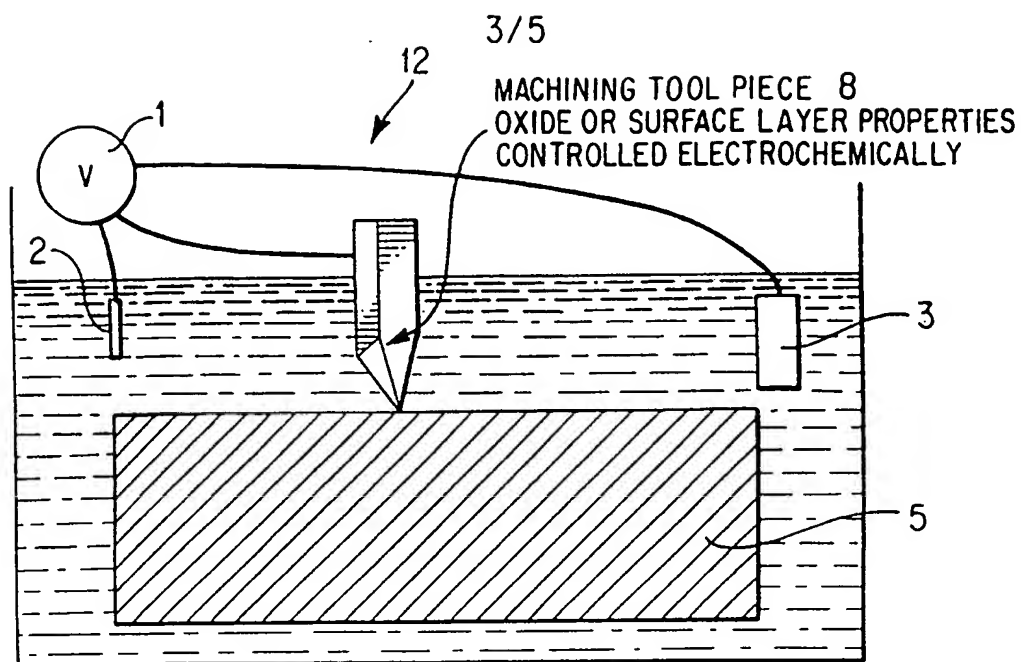


FIG. 3(a)

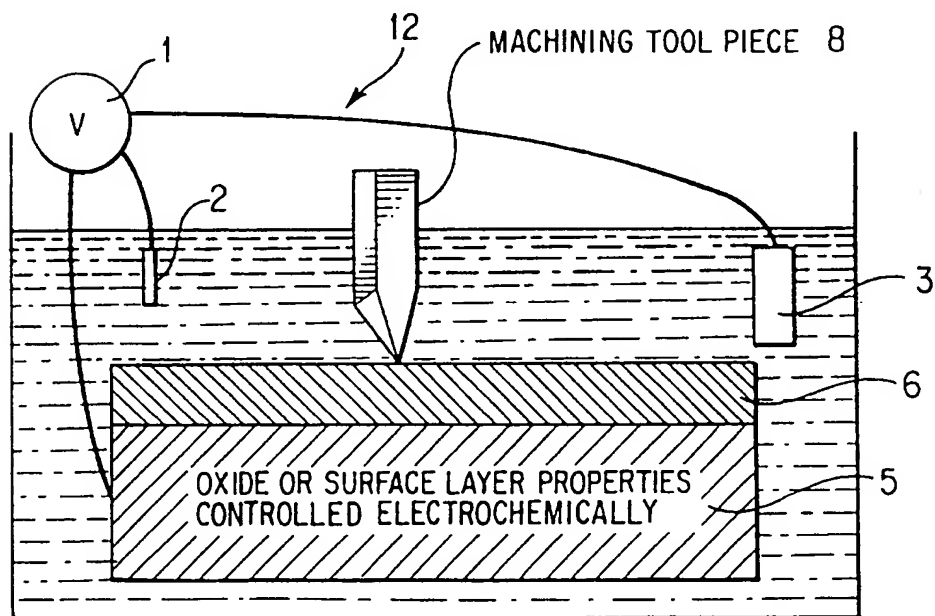


FIG. 3(b)

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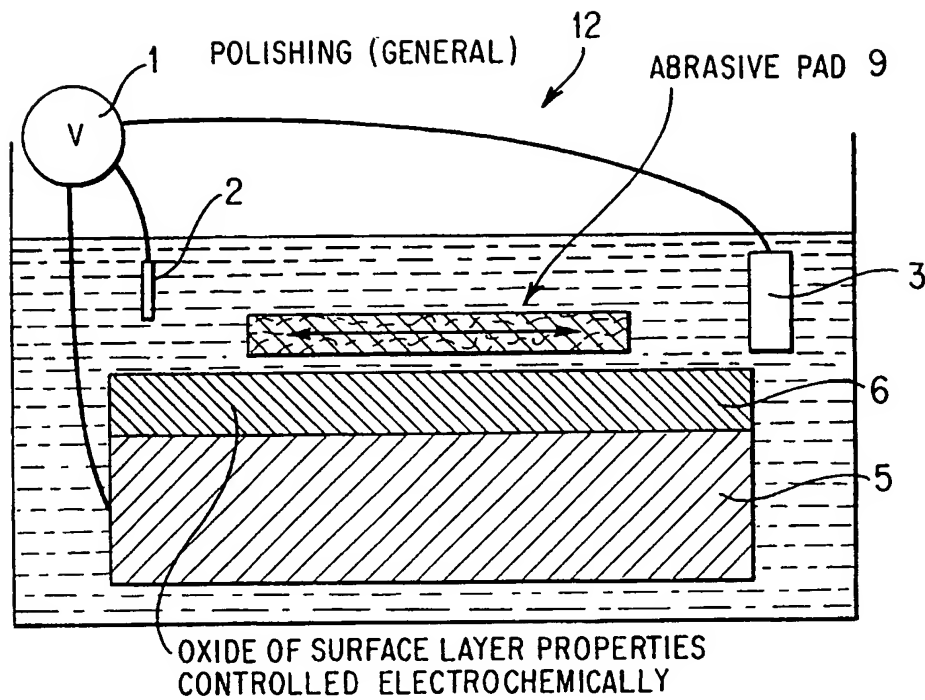


FIG. 4

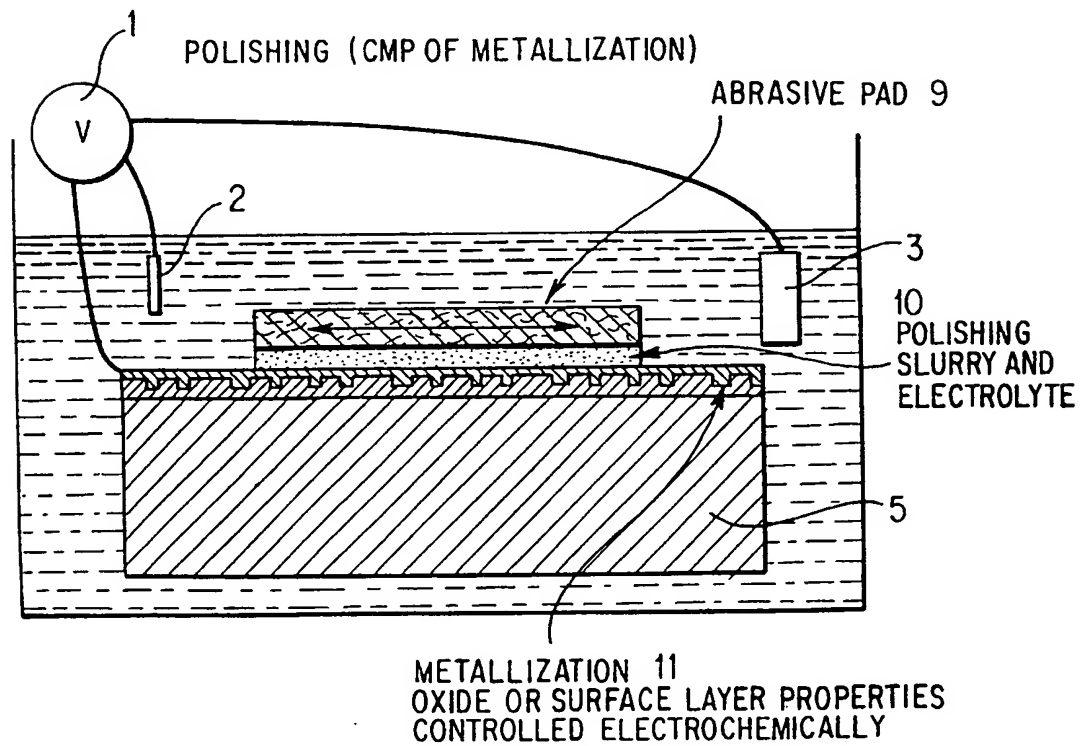


FIG. 5(a)



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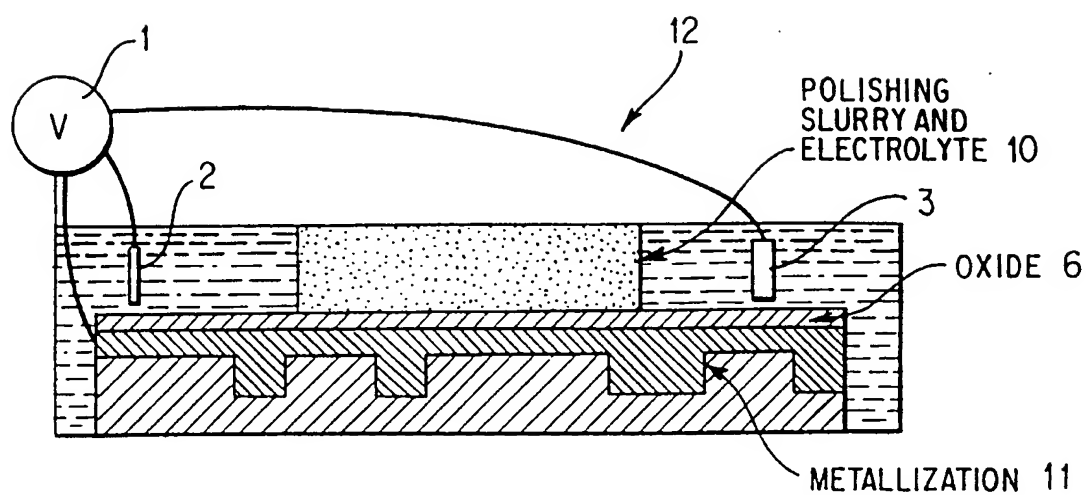


FIG. 5(b)

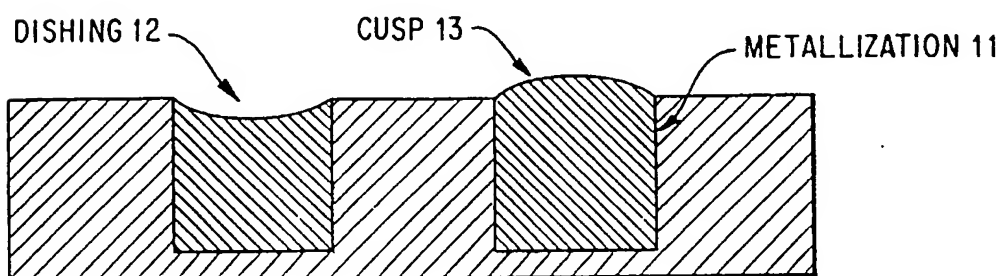


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/25045

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B24B 1/00; B23H 5/04; H01L 21/304

US CL : Please See Extra Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/345LP; 204/224M; 205/662,663; 216/38, 88, 89; 438/692, 693

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

chemical-mechanical polishing, planarize

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 4,839,005 A (KATSUMOTO et al) 13 June 1989 (13-06-89), abstract, column 6, lines 28-44.	1-6, 15, 17, 18 ----- 8, 9
X	US 4,956,056 A (ZUBATOVA et al) 11 September 1990 (11-09-90), abstract.	1, 6, 10, 15, 16, 17
Y -- A	US 5,562,529 A (KISHII et al) 08 October 1996 (08-10-96), abstract, column 5, line 61 to column 6, line 7.	1-9, 15, 17, 18 ----- 11-14, 19, 20

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

WILLIAM LEADER

Telephone No. (703) 308-0661

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/25045

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y -- A	US 5,575,706 A (TSAI et al) 19 November 1996 (19-11-96), abstract, column 3, lines 53-65.	1-9, 15, 17, 18 ----- 11-14, 19, 20
X -- Y	US 5,639,363 A (OHMORI et al) 17 June 1997 (17-06-97), abstract, column 2, lines 4-11, column 10, lines 35-41.	1-7, 10, 15, 16, 17 ----- 8, 9
Y	LOWENHEIM, F. A. Electroplating. New York: McGraw-Hill Book Company. 1978, pages 137-139.	8, 9

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## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

156/345LP; 204/224M; 205/662,663; 216/38, 88, 89; 438/692, 693; 451/36, 287, 288